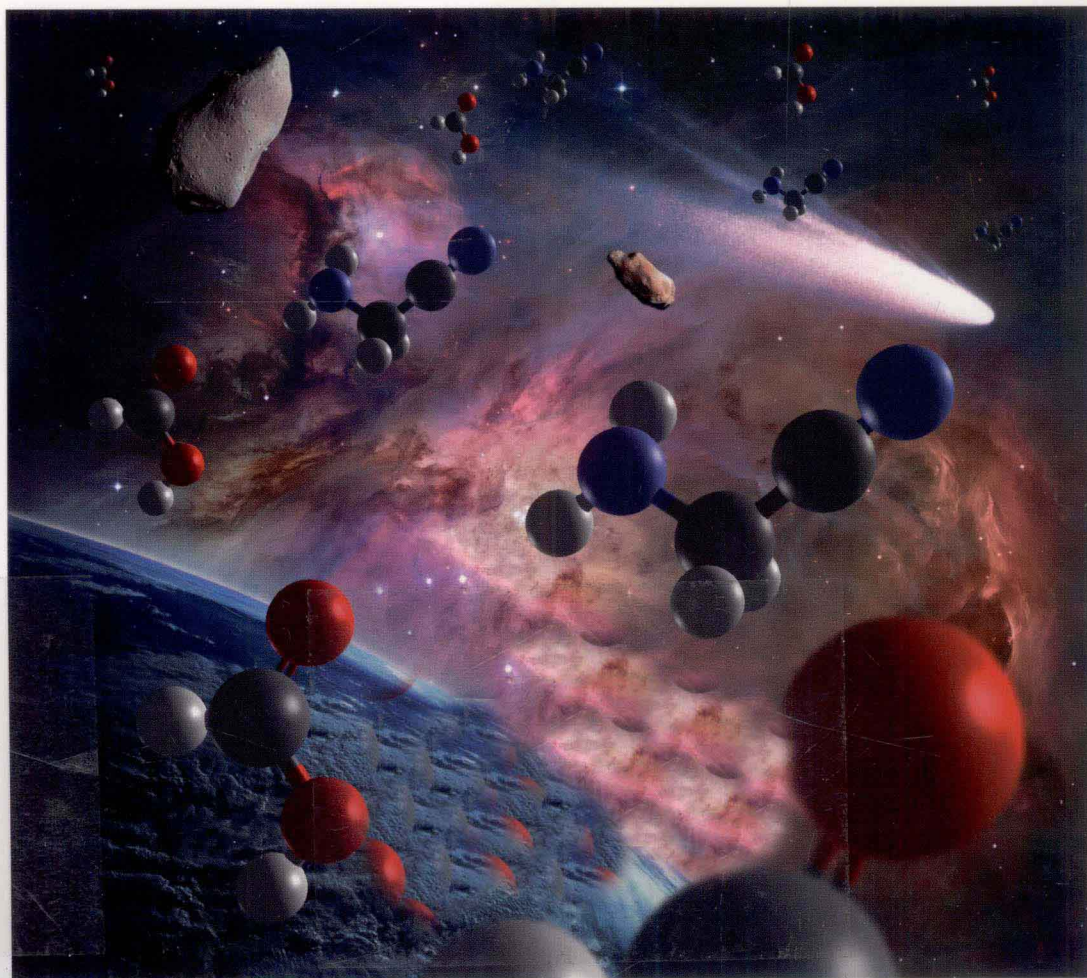


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Chemistry in Space

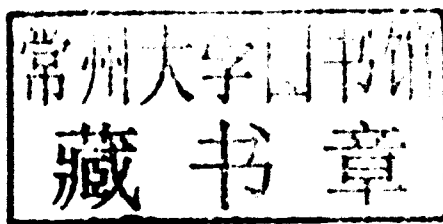
From Interstellar Matter to the Origin of Life



Dieter Rehder

Chemistry in Space

From Interstellar Matter to the Origin of Life



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Cover

The molecules shown on the cover are formic acid and aminoacetonitrile. Both have recently been discovered in interstellar clouds.

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Preface

On 27th December 1984, a team of “meteorite hunters,” funded by the National Science Foundation, picked up a rock of 1.93 kg in an Antarctic area known as Alan Hills. Since it was the first one to be collected in 1984, it was labeled ALH84001, *ALan Hills 1984 no. 001*. Soon it became evident that this meteorite originated from our neighbor planet Mars—a rock that formed 4.1 billion years ago and was blasted off the red planet’s crust 15 million years ago by an impacting planetesimal. After roaming about in the Solar System for most of its time, this rock entered into the irresistible force of Earth’s attraction, where it landed 13 thousand years ago, in Antarctica and hence in an area where it was protected, at least in part, from weathering. Structural elements detected in this Martian meteorite, considered to represent biomarkers, sparked off a controversial debate on the possibility of early microbial life on our neighbor planet about 4 billion years ago, and shipping of Martian life forms to Earth, a debate which became reignited by recent reinvestigations of the meteoritic inclusions.

Other meteorites, originating from objects in the asteroid belt between Mars and Jupiter, have brought amino acids and nucleobases to Earth, among these amino acids which are essential for terrestrial life forms. Does this hint toward an extraterrestrial origin of at least part of the building blocks necessary for terrestrial life? And if yes—how could amino acids, which are rather complex molecules, have been synthesized and survived under conditions prevailing in space?

The idea of “seeds (*spermata*) of life,” from which all organisms derive, goes back to the cosmological theory formulated by the Greek philosopher and mathematician Anaxagoras in the 5th century B.C. Anaxagoras, perhaps better known for his “squaring the circle,” thus may be considered the originator of what became established as *panspermia*. Panspermia reached the level of a scientific (and popular) hypothesis in the 19th century through contributions from Berzelius, Pasteur, Richter, Thomson (Lord Kelvin), von Helmholtz, and others, a hypothesis according to which life originated and became distributed somewhere in space, and was transported to the planets from space. In 1903, the Swedish chemist Arrhenius proposed that radiation pressure exerted by stars such as our Sun can spread submicrometer to micrometer-sized “spores of life,” a proposal that later (in the 1960s) was quantified by Sagan. The panspermia hypothesis got somewhat disreputable, when Francis H. Crick (who, together with Watson, received the

1962 Nobel Prize in Medicine for the discovery of the double-helix structure of deoxyribonucleic acid) and Leslie Orgel published a paper, in 1973, where they suggested that life arrived on Earth through “directed panspermia,” where *directed* refers to an extraterrestrial civilization. The likeliness of another civilization somewhere else out in space is even more speculative than the likeliness that Life came into existence at all.

There is no doubt, of course, that life exists on Earth. Whether Earth is the cradle of life (from which it may have been transported elsewhere into our Solar System or even beyond) or whether life has been carried to our planet from outside (exospermia) remains an interesting concern to be addressed. ALH84001 may provide a clue to this question. The discovery of exoplanets (planets orbiting other stars than our Sun in the Milky Way galaxy) is another issue that stimulates imagination as it comes to the possibility of extraterrestrial life. New exoplanets are being discovered at a vertiginous speed, and a few of the about 455 exoplanets known to date, so-called super-Earths, do have features which are reminiscent of our planet.

Hamburg, May 2010

Dieter Rehder

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1

Introduction and Technical Notes

In the year 1609, Johannes Kepler published a standard work of astronomy, the *Astronomia Nova, seu Physica Coelestis, tradita commentariis de Motibus Stellæ Martis*: “The New Astronomy, or Celestial Physics, based on records on the Motions of the Star Mars.” In Chapter LIX (59), he summarizes what became known as Kepler’s first and second law (Figure 1.1). The heading of this chapter starts as follows: *Demonstratio, quod orbita Martis ... fiat perfecta ellipsis*: “This is to demonstrate that the Martian orbit ... is a perfect ellipse,” or—in today’s common phrasing of Kepler’s first law: “The planet’s orbit is an ellipse, with the Sun at one focus.” The second law states that the “line connecting the Sun and the planet sweeps out equal areas in equal time intervals.” (The third law was formulated 10 years later: $p_1^2/p_2^2 = r_1^3/r_2^3$, p = revolutionary period, r = semimajor axis; the lower indices 1 and 2 refer to two planets.) Kepler’s pioneering mathematical treatise, based on minute observations collected by Tycho Brahe, had been a breakthrough for astronomy, and applications of his laws are still influential in modern astronomy.

A second trailblazing event 400 years ago was the discovery of what is now known as the “Galilean moons,” the four large moons of the planet Jupiter. Galileo Galilei announced the discovery of three of the Jovian moons on the 7th of January 1610 (discovery of the fourth moon followed a couple of weeks later)—according to the Gregorian calendar, which corresponds to the 28th of December, 1609, in the Julian calendar. In honor of his mentor Cosimo II de Medici, Galilei named the moons *Cosmica Sidera* (Cosimo’s stars), and then *Medicea Sidera* (stars of the Medici). Following a suggestion by Simon Mayr (or Simon Marius in the Latinized version) in 1614, the four moons were termed “Io, Europa, Ganymed *atque* (and) Callisto lascivo nimivm perplacvere Iovi” (... who greatly pleased lustful Jupiter [Zeus]). Simon Mayr discovered the moons independently of Galilei, but announced his discovery a day later, on the 8th of January 1610. The discovery of the moons, and realization that the moons orbit *Jupiter*, was a final bash against a geocentric worldview of the Universe dominating medieval times.

The two discoveries became duly commemorated in the 2009 International Year of Astronomy, which was also the year for a couple of key discoveries in astronomy, astrophysics, astrochemistry, and astrobiology: (i) detection of the first exoplanets with physical and chemical characteristics approximating those of our home planet;

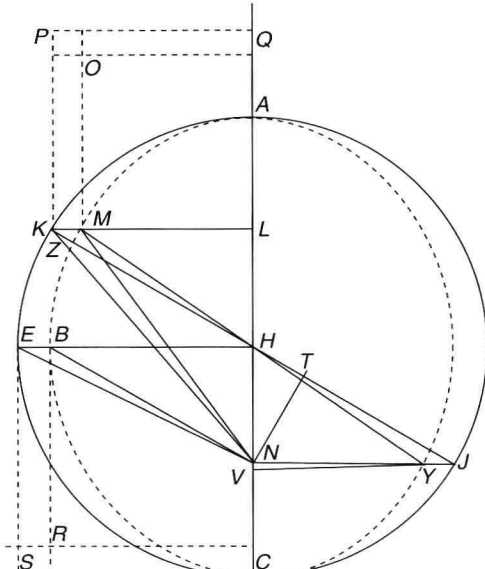


Figure 1.1 Kepler's illustration of his findings on Mars' motions, which became known as Kepler's first and second law of planetary motion; from chapter *LIX* of *Astronomia Nova*, published 1609. The first law states that the planet's orbit is an

ellipse—the punctuated line starting with the quadrant AMB, with the Sun (N) at one focus. The second law provides information on the area (BMN) swept by the line (MN, BN) connecting the Sun and the planet.

(ii) reinvestigation of nanosized magnetite crystals, possible biomarkers, in a Martian meteorite recovered in Antarctica in 1984 (see also Preface); (iii) discovery of the glycine precursor aminoacetonitrile (see cover of this book) in the “Large Molecular Heimat,” a dense interstellar molecular cloud in the constellation of Sagittarius; (iv) the final proof that our next neighbor in the Cosmos, our Moon, contains sizable reservoirs of water, possibly of cometary origin, deposited in permanently shaded craters; and (v) location of the most distant and oldest object in the Universe, a gamma ray burst associated with a stellar-sized black hole or magnetic neutron star, which formed just 630 million years after the Big Bang, the event which is considered the hour of birth of our Universe, 13.7 billion years ago.

These are just a few selected highlights, supposed to adumbrate the scope of the present treatise, and to be addressed together with other topical and less recent events and discoveries in some detail in this book. The book will focus on aspects in astronomy related to chemistry—in stars and the interstellar medium, in the atmospheres, on the surfaces, and in subsurface areas of planets, planetoidal bodies, moons, asteroids, comets, interplanetary, and interstellar dust grains. A topical point to be covered is the query of the origin of life, either on Earth or somewhere else in our Milky Way galaxy, and the genesis of basic molecules functioning as building blocks for complex molecules associated with life and/or

representing life. Along with these chemistry-related issues, general cosmological aspects related to astronomy and astrophysics, and often indispensable for an axiomatic comprehension of chemical processes, will be approached. Some knowledge of the basics of chemical (including bio- and physicochemical) coherency will be afforded to become involved: the book is designed so as to be both an introduction for the interested beginner with some basic knowledge, and a compendium for the more advanced scientist with a background in chemistry and adjacent disciplines.

Several of the crucial points covered in the present book have been treated in book publications by other authors, usually with another target course, that is, less intimately directed toward chemical and biological aspects of astronomical problems. The following glossary (sorted chronologically) is a selection of books and compendia that have animated me during the bygone two decades, and are thus recommended as “Further Reading”.

- Duley, W.W., Williams, D.A. (1984) *Interstellar Chemistry*, Academic Press, London.
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- Thielens, A.G.G.M. (2005) *The Physics and Chemistry of the Interstellar Medium*, Cambridge University Press, Cambridge.
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- Kwok, S. (2007) *Physics and Chemistry of the Interstellar Medium*, University Science Books, Sausalito, CA.
- Shapiro, S.L., Teukolsky, S.A. (2007) *Black Holes, White Dwarfs, and Neutron Stars*, Wiley VCH, Weinheim.

Scientists enrooted in astronomy do have their subject-specific nomenclature and system of units, which is not always easily accessible to a chemist. As an

Table 1.1 Units for concentration and density, and their conversion into molar units.

Quantity	Description	Unit ^{a)}	Molar unit; conversion factor ^{b)}
Column density, column amount, column abundance N	The number of elementary entities in a vertical column. Column: In atmospheric chemistry the height of the atmosphere; ^{c)} in interstellar chemistry the length of the line of sight between observer and a light-emitting (stellar) object	cm^{-2}	$\text{mol m}^{-2};$ $N \times (6.022 \times 10^{19})^{-1}$
Volume(tric) or number density n	The number of elementary entities per unit volume	cm^{-3}	$\text{mol l}^{-1};$ $n \times (6.022 \times 10^{20})^{-1}$
Fractional or abundance ratio $f(X)^d) = n(X)/n(\text{H}_2)$	The number of entities X per number of H_2 molecules	–	–
Molar concentration c	Number of moles per liter of solvent	$\text{M} \equiv \text{mol L}^{-1}$	–
Mixing ratio (mole fraction) $c_X = n_X/\Sigma n_i$	The number of moles of a species X in the overall mix (containing i components); $\Sigma c_X = 1$	–	–

a) Number of elementary entities (atoms, ions, molecules, electrons, ...) per area (cm^{-2}) or volume (cm^{-3}); the number of entities is a dimensionless quantity.

b) Contains the Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ elementary entities (i.e., 1 mol).

c) See Eq. (5.9) in Section 5.2.3.2 for additional details.

d) This symbol is also used for mole fraction.

example, if it comes to the term “concentration” (of a specific species X in a mix), chemists use to think in terms of “molarity” (moles of X per liter of the mix) or “molality” (moles of X per kg), where “mole” relates to the amount of substance: 1 mole of *any* substance is equal to 6.022×10^{23} elementary entities. Examples for elementary entities are elementary particles (such as electrons, protons, and neutrons), atoms, ions, molecules, light quanta. In contrast, astronomers commonly refer to concentration in terms of “column density/abundance/amount,” “fractional density,” and “number/volume density,” conceptions so uncommon for chemists that they hardly do associate any perception with these quantifications. From a chemist’s point of view, *column amount* quoted in terms of mol m^{-2} (i.e., employing the units of the *Système Internationale*, the SI system) is “correct” [1] and has been used wherever sensibly applicable—together with the units preferred by astronomers. Table 1.1 provides an overview of conversions of units for “concentration,” frequently employed in astronomical and astrophysical articles, into

molar units. Conversions will also be provided in the main text wherever this appears to be reasonable.

Most of the units employed in this book are SI units. Where our conceptions from everyday experience are dominated by more classical units, both the SI and the popular units are provided. Examples are temperature (in Kelvin or degrees Celsius), pressure (in Pascal or bar), strength of the magnetic field (the B field; in Tesla or Gauss). Distances in astronomical dimensions, when expressed in meters or 10^3 multiples thereof, are not easily handled by our spatial perception. Astronomical units (AUs), parsecs (pc), and light-years (ly), as defined in Figure 5.2 and Table 5.3, are more easily comprehended and therefore used throughout. Similarly, if it comes to “astronomical ages,” years (a, derived from the Latin *annum*) and multiples thereof, such as megayears ($\text{Ma} = 10^6 \text{ a}$) and gigayears ($\text{Ga} = 10^9 \text{ a}$) are employed rather than the SI unit “second.” Finally, masses (m , SI unit: g) are quoted, were appropriate, in m_{\oplus} (multiples of Earth; \oplus is the astronomical symbol for Earth), m_{J} (multiples of Jupiters) and m_{\odot} (multiples of Suns; \odot is the symbol for the Sun). The lower case letter “m” otherwise stands for magnitude (of a star); the *capital* letter M ($\equiv \text{mol l}^{-1}$) denotes molarity and, in chemical equations, “metal” (all elements beyond helium), while M (in italics) indicates “molecular mass” (g mol^{-1}) [and matrix in reactions on dust particles].

The quantification of “energy” is another point of potential controversy: in chemistry, the (almost exclusive) unit for energy is kilo-Joule per mole (kJ mol^{-1}). In particle physics, this unit is unhandy, and electron volts (eV) are preferred; in spectroscopy, it is common to measure energy in reciprocal centimeters (cm^{-1}) which, strictly speaking, is not energy but energy divided by hc (the product of the Planck constant and the speed of light). Conversions of these units will be provided in the main text wherever appropriate.

References

- 1 Basher, R.E. (2006) Units for column amounts of ozone and other atmospheric gases. *Quart. J. R. Meteorol. Soc.*, **108**, 460–462.

2

Origin and Development of the Universe

2.1

The Big Bang

The dark sky against which we see stars and galaxies is not completely black. Rather, the Universe is filled with a relic electromagnetic radiation called cosmic microwave background (CMB) radiation, characterized by a frequency of 160.2 GHz, corresponding to a wavelength of 1.9 mm. This radiation represents the cosmologically red-shifted (shifted to longer wavelengths, also termed “Doppler shift”) radiation of an incessantly expanding Universe. The intensity to wavelength distribution of the CMB follows an almost perfect black body radiation at a temperature of 2.725 K, and it is almost isotropic, that is, of equal intensity in all directions. Backward extrapolation in time reveals that this background radiation originates from the time where the Universe was 380 000 years old: the time span which elapsed since the Universe started to develop from a singularity in time and space, the starting point of which was termed the “Big Bang.” A spacetime (or gravitational) singularity is, according to the general theory of relativity, the initial state of the Universe. 380 000 years after this development started, the Universe was sufficiently cold, about 3000 K (corresponding to energy of 0.25 eV), to allow for the formation of neutral atoms which no longer absorbed photons, making the Universe transparent. Along with the background radiation, the relative abundance of the stable hydrogen isotopes ^1H (protium) and ^2H (deuterium), and the helium isotopes ^3He and ^4He in the Universe provide a convincing back-up of the present theory.

What became known as the Big Bang theory for the origin of the Universe was originally proposed by Georges Lemaître (1927–1931), who called this theory “hypothesis of the primeval atom,” where “primeval atom” refers to a single point at time $t = 0$ or, rather, to a situation where time and space did not yet exist. The term “Big Bang” goes back to Fred Hoyle (1949) who, incipiently, tried to discredit the hypothesis he was not yet ready to subscribe to. The discovery of the cosmic background radiation in 1964 secured the theory. The “Big Bang event” nowadays is commonly not restricted to the very first fraction of a second where the singularity became resolved, developing into matter, time and space, but to the first few minutes of expansion and evolution of the primordial matter, which includes Big Bang nucleosynthesis. The first about 5 min of the time line, starting 13.73 billion